Spatial and Temporal Patterns in Petrogenic Organic Carbon Mobilisation
during the Paleocene-Eocene Thermal Maximum

E. H. Hollingsworth1*, F. J. Elling2,3, M. P. S. Badger4, R. D. Pancost5, A. J. Dickson4,6, R. L. Rees-Owen5, N. M. Papadomanolaki7,8, A. Pearson2, A. Sluijs7, K. H. Freeman9, A. A. Baczynski9, G. L. Foster1, J. H. Whiteside1,10, and G. N. Inglis1*

1 School of Ocean and Earth Science, University of Southampton, Southampton, UK
2 Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
3 Leibniz-Laboratory for Radiometric Dating and Isotope Research, Christian-Albrechts, University of Kiel, Kiel, Germany
4 School of Environment, Earth and Ecosystem Sciences, The Open University, Milton Keynes, UK
5 Department of Earth Sciences and School of Chemistry, University of Bristol, Bristol, UK
6 Centre of Climate, Ocean and Atmosphere, Department of Earth Sciences, Royal Holloway University of London, Surrey, UK
7 Department of Earth Sciences, Utrecht University, Utrecht, Netherlands
8 Now at Institute für Geologie und Paläontologie, Universität Münster, Münster, Germany
9 Department of Geosciences, The Pennsylvania State University, State College, PA, USA
10 Now at Department of Earth and Environmental Sciences, San Diego State University, San Diego, CA, USA

*Corresponding author: Gordon N. Inglis (Gordon.inglis@soton.ac.uk) and Emily H. Hollingsworth (e.hollingsworth@soton.ac.uk)
Key Points:

- We assess spatial and temporal patterns in petrogenic organic carbon (OC$_{petro}$) mobilisation during the PETM

- Enhanced OC$_{petro}$ mobilisation in the subtropics and mid-latitudes, likely due to an increase in extreme rainfall events

- Mobilisation of OC$_{petro}$ remained elevated during the recovery phase of the PETM
Abstract
The Paleocene-Eocene Thermal Maximum (PETM) was a transient global warming event recognised in the geologic record by a prolonged negative carbon isotope excursion (CIE). The onset of the CIE was the result of a rapid influx of $^{13}$C-depleted carbon into the ocean-atmosphere system. However, the mechanisms required to sustain the negative CIE remains unclear. Previous studies have identified enhanced mobilisation of petrogenic organic carbon ($OC_{petro}$) and argued that this was likely oxidised, increasing atmospheric carbon dioxide ($CO_2$) concentrations after the onset of the CIE. With existing evidence limited to the mid-latitudes and subtropics, we determine whether: (i) enhanced mobilisation and subsequent burial of $OC_{petro}$ in marine sediments was a global phenomenon; and (ii) whether it occurred throughout the PETM. To achieve this, we utilised a lipid biomarker approach to trace and quantify $OC_{petro}$ burial in a global compilation of PETM-aged shallow marine sites ($n = 7$, including five new sites). Our results confirm that $OC_{petro}$ mass accumulation rates (MARs) increased within the subtropics and mid-latitudes during the PETM, consistent with evidence of higher physical erosion rates and intense episodic rainfall events. The high-latitude sites do not exhibit distinct changes in the organic carbon source during the PETM. This may be due to the more stable hydrological regime and/or additional controls. Crucially, we also demonstrate that $OC_{petro}$ MARs remained elevated during the recovery phase of the PETM. Although $OC_{petro}$ oxidation was likely an important positive feedback mechanism throughout the PETM, we show that this feedback was both spatially and temporally variable.

Plain Language Summary
The Paleocene-Eocene Thermal Maximum (PETM) was the most severe global warming event of the last 66 million years, caused by natural and rapid release of greenhouse gases into the atmosphere. However, scientists have been unable to determine why the PETM lasted for > 100,000 years. Several theories suggest further emission of greenhouse gases from positive feedback mechanisms triggered by early onset warming. Here, we explore one such mechanism: $CO_2$ released from the erosion, transport, and oxidation of ancient rock-derived (or petrogenic) organic carbon, and identify if it occurred globally and/or throughout the PETM. We achieve this by looking at biomarkers (molecular fossils) and use this approach to trace the input of
petrogenic organic carbon into the marine realm. Results suggest enhanced transport of petrogenic organic carbon was restricted to the subtropics and mid-latitudes, with limited changes in the high-latitudes. We also find evidence for erosion and transport of petrogenic organic carbon throughout the PETM. Therefore, this process likely contributed to increasing atmospheric CO$_2$ levels and may have been an important positive feedback mechanism in past and future warm climates.

1 Introduction

Climate and tectonics have modulated the flux of carbon to and from terrestrial reservoirs over geological timescales. Early studies predominantly focused on understanding the role of inorganic carbon, for example, carbon dioxide (CO$_2$) released from solid Earth degassing versus CO$_2$ drawdown from silicate weathering (e.g., Berner et al., 1983; Caldeira & Berner, 1997; Walker et al., 1981). However, the past two decades have highlighted the importance of the terrestrial organic carbon cycle as a climate feedback mechanism (Hilton & West, 2020). Whether it acts as a positive or negative feedback mechanism largely depends on whether the organic carbon is ‘biospheric’ (OC$_{bio}$), representing relatively recent thermally immature organic carbon (10$^2$–10$^4$ years old; e.g., vegetation and soils), or ‘petrogenic’ (OC$_{petro}$), representing ancient rock-derived and thermally mature organic carbon (> 10$^6$ years old; e.g., organic carbon-rich shales). Erosion, mobilisation, and the subsequent burial of OC$_{bio}$ in marine sediments sequesters CO$_2$ (Berhe et al., 2007; Stallard, 1998). In contrast, exhumation and oxidation of OC$_{petro}$ during lateral transport from land-to-sea can release CO$_2$ (Petsch et al., 2000). Observations on modern fluvial systems suggest that the fraction of OC$_{petro}$ oxidised positively correlates with the transit duration (Hilton & West, 2020). Up to ~90 % of OC$_{petro}$ is oxidised in large catchments, such as the Amazon and Himalayan range (e.g., Bouchez et al., 2010; Galy et al., 2008), whereas a lower proportion (~10–40 %) of OC$_{petro}$ is oxidised in mountain basins with steep rivers (e.g., Hilton et al., 2011, 2014). Thus, regardless of catchment dynamics, OC$_{petro}$ has the potential to be oxidised and increase atmospheric CO$_2$ concentrations.

Several studies have quantified the mobilisation and burial of OC$_{petro}$ in modern systems (e.g., Blair et al., 2003; Clark et al., 2017, 2022; T. I. Eglinton et al., 2021 and references therein; Galy et al., 2007, 2015 and references therein; Hilton et al., 2010, 2011; Hilton & West, 2020 and...
references therein; Smith et al., 2013) and Holocene sediments (e.g., Hilton et al., 2015; Kao et al., 2008, 2014). While there is a bias towards environments where erosion and transport of terrestrial organic carbon is largely controlled by geomorphic processes, climate is also seen as a strong regulator (e.g., T. I. Eglinton et al., 2021; Hilton, 2017). For example, extreme rainfall events can trigger bedrock landslides (e.g., Hilton et al., 2008) and/or create deeply incised gullies (e.g., Leithold et al., 2006), both of which can increase the quantity of $\text{OC}_{\text{petro}}$ transferred and exposed to atmospheric oxidation. Although, the resulting high abundance of clastic sediments from hyperpycnal flows and turbidites may also enhance the preservation of $\text{OC}_{\text{petro}}$ (e.g., Bouchez et al., 2014; Hilton et al., 2011). As climate model simulations indicate an intensification of the hydrological cycle in response to rising atmospheric CO$_2$ levels and global temperatures (Lee et al., 2021), the delivery of $\text{OC}_{\text{petro}}$ to the oceans will likely be enhanced in the future. However, such predictions are based on present-day observations and/or past climate states that span a lower-than-modern atmospheric CO$_2$ values.

In contrast, the geological record enables investigations into high CO$_2$ states of the past, providing unique insights on how terrestrial carbon cycle processes may operate in the future. Many studies have focused on the Paleocene-Eocene Thermal Maximum (PETM; ~56 million years ago) (McInerney & Wing, 2011), a transient global warming event (e.g., mean surface temperature increase of ~4–6 ºC; Inglis et al., 2020; Tierney et al., 2022) associated with an intensified hydrological cycle (Carmichael et al., 2017 and references therein). The PETM is identified in the geologic record by a negative carbon isotope excursion (CIE) (e.g., -4 ± 0.4 ‰; Elling et al., 2019). The onset of the PETM is on the order-of-millennia (Kirtland Turner, 2018; Zeebe et al., 2014) and is followed by sustained low and stable carbon isotope ($\delta^{13}\text{C}$) values for ~94–170 thousand years (kyrs) (Zeebe & Lourens, 2019), referred to as the “body” of the CIE (Bowen et al., 2006). The body is then followed by a long recovery of ~50–120 kyrs (Bowen, 2013; Murphy et al., 2010; Zeebe et al., 2009), which is further divided into Phase I (initial rapid rise in $\delta^{13}\text{C}$) and Phase II (final gradual rise in $\delta^{13}\text{C}$) (Röhl et al., 2007).

The onset of the CIE was the result of a rapid influx of $^{13}$C-depleted carbon from one or more reservoirs outside the active global exogenic carbon pool (Dickens et al., 1997). Proposed
reservoirs include submarine methane hydrates (Dickens, 2011; Dickens et al., 1995), terrestrial organic carbon (Bowen, 2013; Deconto et al., 2012; Kurtz et al., 2003), and volcanic carbon related to the North Atlantic Igneous Province (Gutjahr et al., 2017; Jones et al., 2019; Storey et al., 2007; Svensen et al., 2004). Less explored are the mechanism responsible for the prolonged body of the CIE. This feature requires continual input of $^{13}$C-depleted carbon (e.g., Zeebe et al., 2009) and several feedback mechanisms (either acting individually or in combination) have been proposed. This includes a slow dissociation of oceanic methane hydrates (Zeebe, 2013) and/or pulsed releases of thermogenic methane from vent complexes (e.g., Frieling et al., 2016; Kirtland Turner, 2018). Alternatively, recent work suggests that CO$_2$ released from OC$_{petro}$ oxidation could explain the extended body of the CIE (Lyons et al., 2019). This theory is based on evidence for an order-of-magnitude increase in the delivery of OC$_{petro}$ to the oceans, ~10–20 kyrs after the onset of the PETM. However, this study was limited to the mid-latitudes (Atlantic Coastal Plain) and subtropics (Tanzania), and thus may not be globally representative. It is also unclear whether enhanced mobilisation of OC$_{petro}$ was a persistent feature throughout the PETM or whether it was restricted to the body interval.

Here we use lipid biomarker thermal maturity ratios to fingerprint OC$_{petro}$ burial in a global compilation of PETM-aged shallow marine sites (n = 7, including five new sites). Lipid biomarkers undergo various structural alterations with increasing thermal maturity (e.g., defunctionalisation, isomerisation, catagenesis, and aromatisation; Peters et al., 2005) and thus can be used to assess the proportion of OC$_{petro}$ in marine sediments (Lyons et al., 2019). We focus on thermally immature, shallow marine sediments as they are ‘hotspots’ for terrestrial organic carbon input (Bianchi et al., 2018). We quantify OC$_{petro}$ burial fluxes before and during the PETM, using a two-endmember mixing model. Overall, we aim to determine whether: (i) enhanced mobilisation and subsequent burial of OC$_{petro}$ in the ocean was a global phenomenon; and (ii) whether it occurred throughout the PETM.

2 Methods

2.1 Data compilation

New n-alkane- and/or hopane-based thermal maturity ratios were acquired from the following PETM-aged shallow marine sites: the International Ocean Drilling Program Expedition 302 Site
M0004A (or the Arctic Coring Expedition; ACEX); the Ocean Drilling Program Site 1172 Hole D (ODP Site 1172); Kheu River; ODP Leg 174AX Ancora Site Hole A/B (Ancora); and the Tanzania Drilling Project Site 14 Hole A (TDP Site 14) (Figure 1 and Table S1 in the supporting information). We also compile n-alkane- and/or hopane-based thermal maturity ratios from the following published PETM-aged shallow marine sites: TDP Site 14 (Carmichael et al., 2017; Handley et al., 2012); South Dover Bridge (SDB) (Lyons et al., 2019); and Cambridge-Dorchester Airport (CamDor) (Lyons et al., 2019).

Figure 1: Location of sites with new data (1-5) and published data (5-7). Paleogeographic reconstructions of 56 million years ago, adapted from Carmichael et al., (2017)

2.2 Organic geochemistry

Samples from ACEX (n = 94), ODP Site 1172 (n = 41), and Ancora (n = 42) were freeze dried, homogenized, and extracted using a MARS5 microwave-assisted extraction system, using: (i) dichloromethane:methanol (DCM:MeOH; 1:1, v:v); (ii) DCM:MeOH (9:1, v:v); and (iii) DCM (see Elling et al., 2019). Each solvent mixture was heated for 30 minutes to 100 °C, followed by a hold time of 20 minutes. The extracts from the three steps were combined into a total lipid extract (TLE) and further divided into five fractions (following Polik et al., 2018). When required, extracted copper was added to the apolar fractions for 24 hours to remove elemental sulphur. The apolar fractions were analysed using a ThermoFisher Trace 1310 GC coupled to a
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Thermo TSQ8000 Triple Quadrupole MS (GC-MS). Helium was used as the carrier gas and separation was achieved with DB-5 column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The GC oven program started at 70 °C for 1 minute, increased to 130 °C at 20 °C min⁻¹, followed by 300 °C at 4 °C min⁻¹, which was then held for 20 minutes. MS scanning occurred between mass-to-charge ratio (m/z) 50 to 650 Daltons, and an ionisation energy of 70 eV. Compound identification was based on: retention times; fragmentation patterns; comparison to an in-house standard; and library matches.

Kheu River samples (n = 39) were extracted at the University of Bristol by ultrasonicating homogenised samples sequentially with DCM, DCM:MeOH (1:1, v:v), and MeOH. Elemental sulphur was removed from the combined TLE using activated copper turnings. An activated silica column with saturated ammonia in chloroform and chloroform:acetic acid (100:1, v:v) was used to separate the neutral and acid fraction, respectively. The apolar fraction was split from the neutral fraction by eluting with hexane:DCM (9:1, v:v) via separation on an alumina column. The apolar fractions were then analysed at the University of Bristol on a Thermoquest Finnigan Trace GC interfaced with a Thermoquest Finnigan Trace MS. The GC was fitted with a fused capillary column (50 m x 0.32 mm i.d.) and the carrier gas was helium. The samples were suspended in ethyl acetate and injected at 70 °C. The temperature program increased to 130 °C (20 °C min⁻¹), then 300 °C (4 °C min⁻¹), and finally remained isothermal for 20 minutes. The MS operated with an electron ionisation source at 70 eV, scanning over m/z ranges of 50 to 850 Daltons. The compounds were quantified on the total ion chromatogram (TIC).

Additional samples (n = 12) from TDP Site 14 were homogenised and extracted at the University of Bristol. Extractions were achieved via Soxhlet apparatus overnight, using DCM:MeOH (2:1 v:v). The apolar fraction was suspended in hexane:DCM (9:1, v:v) and separated by alumina column chromatography. Co-eluting compounds and/or unresolved complex mixtures were reduced with urea adduction (following Pancost et al., 2008). Elemental sulphur was removed using extracted copper turnings. The apolar fractions were analysed at the University of Bristol on the same GC-MS as used for Kheu River. The GC was fitted with a CPsil-5CB column (Agilent Technologies, dimethylpolysiloxane stationary phase) and the carrier gas was helium.
The samples were injected in ethyl acetate at 70 °C. The temperature program increased to 130 °C (20 °C min⁻¹), then 300 °C (4 °C min⁻¹), and finally held for 25 minutes. The MS operated with an electron ionisation source at 70 eV, scanning over m/z ranges of 50 to 850 Daltons.

2.3 Lipid biomarker proxies

2.3.1 n-alkane-based thermal maturity ratios

Modern plants and sediments contain long-chain n-alkanes with an odd-over-even preference (G. Eglinton & Hamilton, 1967), however this is progressively lost during diagenesis. The shift away from a dominance of long-chain n-alkanes with an odd-over-even predominance is captured by the carbon preference index (CPI) (Bush & McInerney, 2013). Modern sediments exhibit high CPI values (> 3–30), indicating relatively unaltered thermally immature organic matter (Diefendorf & Freimuth, 2017). In contrast, mature organic matter (e.g., coal, oil) exhibits low CPI values (~1). CPI values < 1 are less common, and typify low-maturity source rocks from carbonates or hypersaline environments. In this study, sites with extensive post-depositional diagenesis were excluded, such that CPI values closer to 1 likely suggests input of allochthonous thermally mature organic matter (e.g., OCpetro). Here, we use the equation as originally defined by Bray & Evans (1961):

\[
\text{CPI} = \frac{1}{2} \left[ \left( \frac{\sum_{\text{odd}}(C_{25-31})}{\sum_{\text{even}}(C_{26-32})} \right) + \left( \frac{\sum_{\text{odd}}(C_{27-33})}{\sum_{\text{even}}(C_{26-32})} \right) \right] \quad \text{(Eq. 1)}
\]

2.3.2 Hopane-based thermal maturity ratios

Hopanes are the diagenetic products of biohopanoids, which are produced by a wide diversity of bacteria and consequently ubiquitous in a range of environments (Kusch & Rush, 2022). The ratios between different hopanes and their various stereoisomers have long been utilised as a thermal maturity proxy in the field of petroleum geochemistry (e.g., Farrimond et al., 1998; Mackenzie et al., 1980). Most of the hopane-based thermal maturity ratios used in this study are normalised (with the exception of Equation 4). Values indicating high thermal maturity likely suggests allochthonous older material (e.g., pre-PETM-aged OCpetro), as sites with post-depositional diagenesis were excluded from this study. We use a multi-ratio approach as each ratio corresponds to different stages of maturity relative to the oil window (i.e., from early diagenesis to the generation of oil), thus enabling insight on the degree of thermal maturation.
(Figure S1 in the supporting information). However, hopane distributions also vary depending on the lithofacies and/or depositional environment (Peters et al., 2005). Therefore without knowledge of the source rock at each locality, comparison between the sites should be undertaken with caution.

With the exception of \textit{Frankia} spp. (Rosa-Putra et al., 2001), all bacteria synthesise hopanoids with a 17β21β configuration. However, this changes to a more stable βα and then αβ configuration during early diagenesis and then peak oil generation, respectively (Farrimond et al., 1998; Mackenzie et al., 1980). The shift from ββ to αβ is expressed via the following equation (sometimes referred in literature as ‘hopanoid isomerisation’):

\[
\frac{\alpha\beta}{(\alpha\beta + \beta\beta)} \quad \text{(Eq. 2)}
\]

Higher thermal maturity is marked by values closer to 1. However, caution should be taken when interpreting sediments with input from peats, as C31 αβ isomers dominate the hopane distribution within acidic wetland environments (Inglis et al., 2018).

The shift from βα (also referred to as moretane; M) to the more stable αβ (also referred to as hopane; H) is assessed via the following equation (sometimes referred in literature as ‘moretane/hopane ratio’):

\[
\frac{\beta\alpha}{(\beta\alpha + \alpha\beta)} \quad \text{(Eq. 3)}
\]

This equation is mostly applied using C30 hopane (e.g., French et al., 2012), although C29 hopane has also been used (Peters et al., 2005). Values closer to ~0 indicate higher thermal maturity and oil generation.

The C29 αβ hopane (also referred to as norhopane; N) is more thermally stable than C30 αβ hopane. This is assessed via the following equation (sometimes referred in literature as ‘norhopane/hopane ratio’):
As well as a thermal maturity proxy, this ratio has been utilised to differentiate between anoxic carbonate and/or marl source rocks (> 1) vs. clay-rich source rocks (< 1) (Peters et al., 2005).

Towards the early stages of oil generation, there is a change in stereochemistry at the C-22 position, from the biologically favoured R configuration to a near equal mix of R and S (Farrimond et al., 1998; Mackenzie et al., 1980; Peters et al., 2005). This is expressed via the following equation (sometimes referred in literature as ‘homohopane isomerisation’):

\[
\frac{S}{S + R} \quad \text{(Eq. 5)}
\]

This equation uses C_{31-35} hopanes (also referred to as homohopanes) and approaches maximum (equilibrium) values of ~0.6 as thermal maturity increases and oil is generated.

At the late stage of oil generation, C_{27} hopanes shift in the position of a D-ring methyl group, from C-18 (17α(H),22,29,30-trisnorhopane; T_m) to C-17 (18α(H),22,29,30-trisnorneohopane; T_s) (Farrimond et al., 1998; Peters et al., 2005). This is expressed via the following equation:

\[
\frac{T_s}{T_s + T_m} \quad \text{(Eq. 6)}
\]

T_m refers to maturable (less stable), whereas T_s denotes stable. Values closer to 1 indicate higher thermal maturity, although the oxicity of the depositional environment also has a notable influence (Peters et al., 2005).

2.4 Two-endmember mixing models

The fraction of OC_{petro} (f_{petro}) was calculated for each hopane-based thermal maturity ratio (X_{mix}; Table 1), following the two-endmember mixing model from Lyons et al. (2019):

\[
X_{mix} = f_{petro} \times X_{petro} + (1 - f_{petro}) \times X_{background} \quad \text{(Eq. 7)}
\]

where X_{background} and X_{petro} is the defined immature and mature endmembers, respectively. The endmembers for C_{31-35} S/(S+R) ratio follow the definitions in Lyons et al. (2019), where X_{background} is the contemporaneous carbon value of 0 and X_{petro} is the most thermally mature value.
of 0.6. The endmembers for C29-30 βα/(βα + αβ) ratio also follow the definitions in Lyons et al. (2019), where \( X_{\text{background}} = 1 \) and \( X_{\text{petro}} = 0 \). For this study, the endmembers of the \( \alpha\beta/(\alpha\beta + \beta\beta) \) ratio was defined as 0 for \( X_{\text{background}} = 1 \) for \( X_{\text{petro}} \). Note that C29 \( \alpha\beta/C30 \alpha\beta \) and \( T_s/(T_s + T_m) \) ratios were excluded due to their strong dependence on the source rock and/or depositional environment (Peters et al., 2005).

Table 1: The hopane-based thermal maturity ratio (\( X_{\text{mix}} \)) used to calculate \( f_{\text{petro}} \), with assumed linear sedimentation rate (LSR) and total organic carbon (TOC) reference for each site

<table>
<thead>
<tr>
<th>Site</th>
<th>( X_{\text{mix}} )</th>
<th>LSR (cm kyr(^{-1}))</th>
<th>TOC references</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-PETM</td>
<td>Core PETM</td>
<td>Recovery PETM</td>
</tr>
<tr>
<td>ACEX(^a)</td>
<td>C30-31 ( \alpha\beta/(\alpha\beta + \beta\beta) )</td>
<td>1</td>
<td>Min: 3.8</td>
</tr>
<tr>
<td></td>
<td>C31 ( S/(S + R) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C30 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODP Site 1172(^b)</td>
<td>C30-31 ( \alpha\beta/(\alpha\beta + \beta\beta) )</td>
<td>0.57</td>
<td>Min: 0.4</td>
</tr>
<tr>
<td></td>
<td>C31 ( S/(S + R) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C30 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kheu River(^c)</td>
<td>C29-31 ( \alpha\beta/(\alpha\beta + \beta\beta) )</td>
<td>0.3</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>C29-30 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ancona(^d)</td>
<td>C30-31 ( \alpha\beta/(\alpha\beta + \beta\beta) )</td>
<td>0.8</td>
<td>11.2 and 4.3</td>
</tr>
<tr>
<td></td>
<td>C31 ( S/(S + R) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C30 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDP Site 14(^e)</td>
<td>C29-31 ( \alpha\beta/(\alpha\beta + \beta\beta) )</td>
<td>Min: 0.5</td>
<td>Max: 2</td>
</tr>
<tr>
<td></td>
<td>C31-35 ( S/(S + R) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C29-30 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td>Min: 3.5</td>
<td>Max: 14</td>
</tr>
<tr>
<td>SDB(^f)</td>
<td>C31 ( S/(S + R) )</td>
<td>Min: 1.03</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>C29 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td>Max: 2.4</td>
<td>Max: 2.4</td>
</tr>
<tr>
<td>CamDor(^f)</td>
<td>C29 ( \beta\alpha/(\beta\alpha + \alpha\beta) )</td>
<td>Min: 1.03</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>C31-32 ( S/(S + R) )</td>
<td>Max: 2.4</td>
<td>Max: 2.4</td>
</tr>
</tbody>
</table>


\(*f_{\text{petro}}\) calculated in Lyons et al. (2019)

2.5 Mass accumulation rates

The mass accumulation rate (MAR; in gC cm\(^{-2}\) kyr\(^{-1}\)) of OC\(_{\text{petro}}\) was recalculated for all the new and published \( f_{\text{petro}} \) data, following Lyons et al. (2019):

\[
\text{MAR} = \text{LSR} \times \rho \times f_{\text{petro}} \times \frac{\text{TOC}}{100} \quad \text{(Eq. 8)}
\]
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where LSR is the linear sedimentation rate (cm kyr$^{-1}$), $\rho$ is the dry bulk density (g cm$^{-3}$), and
TOC is the total organic carbon (%). A constant $\rho$ value of 1.8 g cm$^{-3}$ was assumed across all the
sites. The TOC values and LSR were acquired for each location from previously published
studies (Table 1). TOC records from ODP Site 1172 (Papadomanolaki et al., 2022) and TDP Site
14 (Aze et al., 2014) were linearly interpolated to match the depths of the biomarker data, using
R Package Astrochron (Meyers, 2014). LSR estimates were obtained (where possible) for three
key time intervals: (i) pre-PETM (Paleocene); (ii) the “core” (onset and body of the CIE) of the
PETM; (iii) and the recovery of the PETM (see Text S1 in the supporting information). This was
available for all the sites with the exception ODP Site 1172, which lacks the recovery interval.
Note that the recovery at Ancora and SDB was further divided into: (iiiia) Phase I; and (iiib)
Phase II. Since Kheu River does not have LSR data, estimates were taken from the nearby
Aktumsuk section (Uzbekistan; John et al., 2008). Both sites comprise shallow marine deposits
that exhibits TOC values from ~0 % pre-PETM to a maximum of ~8.5 % during the PETM
(Bolle et al., 2000; Dickson et al., 2014). Similarly, LSRs from within the core interval of SDB
was assumed to be the same for the entire PETM section at CamDor (following Lyons et al.,
2019).

3 Results

3.1 Thermal maturity ratios

3.1.1 ACEX

The apolar fraction contains short- (C$_{15}$-$C_{19}$), mid- (C$_{21}$-$C_{25}$), and long- (C$_{27}$-$C_{33}$) chain n-alkanes, and
C$_{27}$ to C$_{32}$ hopanes (including $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ isomers). Both CPI (ranging from ~1–3) and
hopane-based thermal maturity ratios exhibit relatively stable trends throughout the sequence,
suggesting that the organic carbon source did not distinctly change (Figure 2). Note that potential
information may be missing due poor core recovery between ~388–384.5 mcd (Sluijs et al.,
2006). However, $C_{30}\alpha\beta/(\alpha\beta + \beta\beta)$, $C_{31}\,S/(S + R)$, and $T_s/(T_s + T_m)$ values slightly increase (i.e.,
higher thermal maturity) between pre-PETM and the core of the PETM, by an average of 0.01,
0.01, and 0.08, respectively. These indices then decline during the recovery interval. $C_{31}\,\alpha\beta/(\alpha\beta + \beta\beta)$
and $C_{30}\beta\alpha/(\beta\alpha + \alpha\beta)$ ratios exhibit the opposite trend, with lower thermal maturity during the
core and the $C_{30}\beta\alpha/(\beta\alpha + \alpha\beta)$ ratio continuing to decline into the recovery.
Figure 2: Thermal maturity ratios at ACEX. Note some of the axis are reversed to reflect increasing thermal maturity towards the right. a) bulk sediment $\delta^{13}C$ of total organic carbon ($\delta^{13}C_{TOC}$) (Elling et al., 2019), b) CPI (this study), c) $\alpha\beta/(\alpha\beta + \beta\beta)$ ratios (this study), d) $S/(S + R)$ ratio (this study), e) $\beta\alpha/(\beta\alpha + \alpha\beta)$ ratio (this study), and f) $T_s/(T_s + T_m)$ ratio (this study).

The PETM interval (including the core and recovery) is highlighted by red shading, and a core gap is present from ~388 to 384.5 mcd (Sluijs et al., 2006)

3.1.2 ODP Site 1172

The apolar fraction contains $C_{16}$ to $C_{34}$ $n$-alkanes and the CPI has a mean value of 2.8. Samples with CPI > 3 (i.e., relatively low thermal maturity), are mostly constrained to the pre-PETM interval (Figure 3). Hopanes range from $C_{27}$ to $C_{32}$ (including $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ isomers), and the thermal maturity ratios exhibit a relatively stable trend throughout the sequence. However, $C_{31}$ $S/(S + R)$ ratio slightly increases by 0.09 during the core and into the recovery of the PETM, suggesting potential input of thermally mature organic carbon. $C_{30}$ $\alpha\beta/(\alpha\beta + \beta\beta)$, $C_{31}$ $\alpha\beta/(\alpha\beta + \beta\beta)$, and $C_{30}$ $\beta\alpha/(\beta\alpha + \alpha\beta)$ values present the opposite behaviour, shifting slightly towards thermally immature values during the core of the PETM, by an average of 0.19, 0.22, and 0.07 respectively. During the recovery, all parameters return to more thermally mature values.
3.1.3 Kheu River

C_{16} to C_{35} n-alkanes were identified in the apolar fraction, in addition to C_{27} to C_{31} hopanes (including αβ, βα, and ββ isomers). Prior to the PETM and during the recovery, the CPI drops below 1, which may suggest input of low-maturity source rocks from carbonates or hypersaline environments. On the other hand, the CPI oscillate drastically between ~1 and ~3 within the lower depths of the core of the PETM (~0–50 cm; Figure 4). This section of high variability is also reflected in the C_{29} αβ/C_{30} αβ and C_{29} βα/(βα + αβ) ratios, suggesting rapid changes in the organic carbon source. However, part of this signal may be biased by greater sampling resolution within the PETM. Overall, the average of all the thermal maturity ratios exhibit lower thermal maturity during the core. In addition, the C_{29} αβ/C_{30} αβ ratio present values > 1 during the
PETM, potentially indicating input from a clay-rich source rock. With the exception of $T_s/(T_s + T_m)$, all of the ratios increase in higher thermal maturity during the recovery to either higher than pre-PETM (i.e., $C_{29} \alpha\beta/(C_{29} \alpha\beta + C_{30} \alpha\beta)$ and $C_{29-30} \beta\alpha/(\beta\alpha + \alpha\beta)$ ratios) or near pre-PETM values (i.e., $C_{29-31} \alpha\beta/(\alpha\beta + \beta\beta)$ ratio).

Figure 4: Thermal maturity ratios at Kheu River. Note some of the axis are reversed to reflect increasing thermal maturity towards the right. a) bulk sediment $\delta^{13}$C of organic carbon ($\delta^{13}$C$_{org}$) (Dickson et al., 2014), b) CPI (this study), c) $\alpha\beta/(\alpha\beta + \beta\beta)$ ratios (this study), d) $C_{29} \alpha\beta/ C_{30} \alpha\beta$ ratio (this study), e) $\beta\alpha/(\beta\alpha + \alpha\beta)$ ratios (this study), and f) $T_s/(T_s + T_m)$ ratio (this study). The PETM interval (including the core and recovery) is highlighted by red shading.

3.1.4 Ancora

The apolar fraction contains $C_{15}$ to $C_{34}$ $n$-alkanes and $C_{27}$ to $C_{31}$ hopanes (including $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ isomers). CPI ranges from 1–2.2 and is stable throughout the record (Figure 5). Similarly, $C_{30}$ $\alpha\beta/(\alpha\beta + \beta\beta)$ values remain relatively constant, albeit exhibiting a very slight decline by an average of 0.01–0.03 (i.e., decreasing thermal maturity). On the other hand, $C_{31} S/(S + R)$ and $C_{30} \beta\alpha/(\beta\alpha + \alpha\beta)$ values peak towards higher thermal maturity during the core of the PETM. The former presents a drastic shift from an absence of the S configuration to a dominance of R,
sugestion potential transient input of thermally mature organic carbon. However, the rise in the two ratios do not occur synchronously, instead $C_{31} S/(S + R)$ values lag behind by ~1.5 mcd.

Figure 5: Thermal maturity ratios at Ancora. Note some of the axis are reversed to reflect increasing thermal maturity towards the right. a) bulk sediment $\delta^{13}C_{TOC}$ of total organic carbon ($\delta^{13}C_{TOC}$) (Elling et al., 2019), b) CPI (this study), c) $\alpha\beta/(\alpha\beta + \beta\beta)$ ratios (this study), d) $S/(S + R)$ ratio (this study), and e) $\beta\alpha/(\beta\alpha + \alpha\beta)$ ratio (this study). The PETM interval (including the core and recovery) is highlighted by red shading.

3.1.5 TDP Site 14

$C_{16}$ to $C_{33}$ $n$-alkanes and $C_{27}$ to $C_{35}$ hopanes (including $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ isomers) were identified in the apolar fraction. The CPI remains > 3 (i.e., low thermal maturity), with the exception of five data points which occur during the core of the PETM (Figure 6). Most noticeable is the large variability in the hopane-based thermal maturity ratios pre-PETM and for the first ~4 m of the core of the PETM. In the upper ~5 m of the core of the PETM, the ratios are more stable and in general agreement. This interval mostly exhibits more thermally mature values than during pre-
PETM section, suggesting a potential shift to an input of thermally mature organic carbon. For example, \(C_{29-31} \alpha \beta / (\alpha \beta + \beta \beta)\) values are close to its mature endmember of 1.

Figure 6: Thermal maturity ratios at TDP Site 14. Note some of the axis are reversed to reflect increasing thermal maturity towards the right. a) bulk sediment \(\delta^{13}C\) of organic carbon (\(\delta^{13}C_{org}\)) (Aze et al., 2014), b) CPI (closed symbols from this study and open symbols from Handley et al., 2012), c) \(\alpha \beta / (\alpha \beta + \beta \beta)\) ratios (closed symbols from this study and open symbols from Handley et al., 2012), d) \(S/(S + R)\) ratios (closed symbols from this study and open symbols from Handley et al., 2012), e) \(C_{29} \alpha \beta / C_{30} \alpha \beta\) ratio (Handley et al., 2012), and f) \(\beta \alpha / (\beta \alpha + \alpha \beta)\) ratios (Handley et al., 2012). The PETM interval (including the core) is highlighted by red shading, and an unconformity truncates the CIE at 12.6 m.

3.2 \(OC_{petro}\) mass accumulation rates

The \(OC_{petro}\) MARs were acquired from all the sites and, following the LSRs, the \(OC_{petro}\) MARs were grouped into the key time intervals at each site (see Text S1 in the supporting information). To enable comparison between sites, we calculated the fold change in mean \(OC_{petro}\) MARs between pre-PETM and during the PETM (i.e., including the core and recovery of the PETM) (Figure 7). Overall, most of the sites (i.e., ACEX, Kheu River, Ancora, SDB, CamDor, and TDP Site 14) display an increase in \(OC_{petro}\) MARs during the PETM. However, the sites with the
largest increase are restricted to the mid-latitudes (i.e., Kheu River, Ancora, and SDB). In contrast, ODP Site 1172 exhibits a small decrease in $OC_{\text{petro}}$ MAR during the PETM.

Figure 7: Log$_{10}$ fold change in mean $OC_{\text{petro}}$ mass accumulation rates (MARs) between pre-PETM and during the PETM (i.e., including the core and recovery of the PETM). The latitudes are defined as: high (> 60° N/S); mid- (30–60° N/S); and subtropics (15–30° N/S) (see Table S1 in the supporting information)

4 Discussion

4.1 Enhanced $OC_{\text{petro}}$ mass accumulation rates in the subtropics and mid-latitudes during the PETM

A previous study from Tanzania (TDP Site 14) reported a relative increase in the thermally mature $\alpha\beta$ hopane during the PETM (Carmichael et al., 2017; Handley et al., 2012). Here, we present new hopane-based thermal maturity data that reveals rapidly fluctuating values within the first ~4 m of the core of the PETM (Figure 6). Similar patterns were observed in the chain-length distributions of $n$-alkanes, the branched and isoprenoid tetraether (BIT) index, bulk sediment $\delta^{13}$C of organic carbon ($\delta^{13}$C$_{\text{org}}$), and the $n$-alkane $\delta^{13}$C record (Aze et al., 2014; Carmichael et al., 2017; Handley et al., 2008, 2012). The latter two was previously suggested to reflect episodic reworking of older (pre-PETM) material rather than changes in the atmospheric carbon reservoir (Figure 6; Aze et al., 2014; Handley et al., 2008). The hopane-based thermal maturity ratios within this study confirms this variable delivery of organic carbon sources, from $OC_{\text{bio}}$ to $OC_{\text{petro}}$.

In contrast, the upper ~5 m of the core of the PETM exhibits more stability in the hopane-based thermal maturity ratios (Carmichael et al., 2017; Handley et al., 2012), $\delta^{13}$C$_{\text{org}}$ values, and $n$-alkane $\delta^{13}$C values (Aze et al., 2014; Handley et al., 2008). The hopane-based thermal maturity
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ratios also present higher thermal maturity, indicating a switch from an episodic to persistent
delivery of OC_{petro} (Carmichael et al., 2017; Handley et al., 2012). During the PETM, the overall
increase in thermally mature hopanes in addition to the LSR drives the OC_{petro} MARs to rise by
an average of 8x10^{-3} gC cm^{-2} kyr^{-1} (Figure 7). This enhanced OC_{petro} MAR is consistent with
evidence of a shift from predominantly marine organic carbon to a terrestrial organic carbon
source (e.g., an increase in the abundance of long-chain n-alkanes produced by vascular plants
and brGDGTs produced by soil bacteria; Carmichael et al., 2017; Handley et al., 2008, 2012).
Whilst there is greater LSR and terrigenous sediment during the PETM, TOC values declined.
This drop was attributed to the larger contributions of clay (Handley et al., 2012). Evidence
includes an abundance of kaolinite, suggestive of intensified physical erosion (John et al., 2012),
and high Li/Al combined with low Na/Al, suggestive of exhumation of older weathered clay.
These additional proxies also suggest processes that support an increase the mobilisation and
accumulation of OC_{petro} during the PETM.

Similar to Tanzania, Ancora exhibits an increase in the average OC_{petro} MARs (by 2x10^{-2} gC cm^{-2}
kyr^{-1}) during the PETM. This value falls within the average OC_{petro} MARs estimated at two other
sites from the Atlantic Coastal Plain (i.e., 6x10^{-2} gC cm^{-2} kyr^{-1} SDB and 8x10^{-3} gC cm^{-2} kyr^{-1}
CamDor; Figure 7). The higher OC_{petro} MAR is largely driven by a shift in LSR from 0.8 cm kyr^{-1}
(pre-PETM) to 11.28 cm kyr^{-1} (PETM) (Table 1; Stassen et al., 2012). Evidence for terrestrial
input to the Atlantic Coastal Plain during the PETM includes a higher abundance of kaolinite
(Gibson et al., 2000), detrital magnetic minerals (Kopp et al., 2009), charcoal, seed pods, and
terrestrial spores (Self-Trail et al., 2017). In addition, there is an increase in the terrestrial aquatic
ratio (TAR; Bourbonniere & Meyers, 1996; Lyons et al., 2019). Indirect evidence includes
changes in the marine microfossil assemblage towards benthic foraminifera (Self-Trail et al.,
2017) and dinoflagellates (Sluijs & Brinkhuis, 2009) that can tolerate brackish water with high
sediment input (Self-Trail et al., 2017). However, with the exception of the abrupt peaks of C_{31}
S/(S + R) at ~169–171 mcd and C_{30} \beta\alpha/(\beta\alpha + \alpha\beta) at ~171–173 mcd, the thermal maturity ratios at
Ancora are relatively stable compared to SDB and CamDor (Figure 5; Lyons et al., 2019).
Furthermore, SDB and CamDor are characterised by a 6 % increase in \delta^{13}C_{org} values during the
PETM (Lyons et al., 2019), which was argued to represent reworking of older (pre-PETM)
material and not an increase in primary production (Lyons et al., 2019). This $^{13}$C enrichment is not observed at Ancora (Figure 5; Elling et al., 2019).

The average OC$_{\text{petro}}$ MAR at Kheu River exhibits an increase (by $3 \times 10^{-2}$ gC cm$^{-2}$ kyr$^{-1}$) during the PETM (Figure 7), driven by an order-of-magnitude rise in TOC values from an average background level of ~0.1% (pre- and post-PETM) to ~4.4% (Dickson et al., 2014). However, in contrast to the sites discussed thus far, Kheu River thermal maturity ratios shift to immature values during the core of the PETM (Figure 4). During the PETM, the $n$-alkane distribution is dominated by long-chain homologues characteristic of vascular plants (Dickson et al., 2014). It can therefore be argued that the shift observed in the thermal maturity ratios is mostly due to enhanced input of the OC$_{\text{bio}}$ (i.e., immature hopanes such as $\beta\beta$ isomers) transported from land, although in situ production cannot be dismissed. In addition, the $\delta^{13}$C$_{\text{org}}$ record does not present $^{13}$C enrichment during the PETM (Figure 4; Dickson et al., 2014). However, an increase in the Chemical Index of Alteration (CIA) and spike in Ti/Al during the PETM not only corroborates terrestrial input but possibly erosion of older (pre-PETM) material (Dickson et al., 2014). As such, both OC$_{\text{petro}}$ and (to a larger extent) OC$_{\text{bio}}$ likely contributed. Therefore, this study highlights the need to quantify OC$_{\text{bio}}$, as any carbon sequestered via OC$_{\text{bio}}$ burial may negate CO$_2$ released via enhanced OC$_{\text{petro}}$ oxidation (e.g., Bowen & Zachos, 2010; John et al., 2008; Kaya et al., 2022; Papadomanolaki et al., 2022; Sluijs, Röhl et al., 2008). Indeed, this was demonstrated to have occurred during the Holocene (e.g., Galy et al., 2015; Hilton et al., 2015; Kao et al., 2014). In conclusion, the subtropical and mid-latitude sites all exhibit an increase in OC$_{\text{petro}}$ MAR during the PETM, and thus may provide an additional source of CO$_2$. However, understanding whether the Kheu River region was a net carbon source or sink requires further investigations.

4.2 Stable organic carbon sources in the high-latitudes during the PETM

In the subtropics and mid-latitudes, average OC$_{\text{petro}}$ MAR increased between $8 \times 10^{-3}$ to $6 \times 10^{-2}$ gC cm$^{-2}$ kyr$^{-1}$ during the PETM for a given site (see Section 4.1). In the high-latitudes, OC$_{\text{petro}}$ MARs in the Arctic (ACEX) and the southwest Pacific Ocean (ODP Site 1172) either increase (by $7 \times 10^{-2}$ gC cm$^{-2}$ kyr$^{-1}$) or decrease (by $3 \times 10^{-4}$ gC cm$^{-2}$ kyr$^{-1}$), respectively (Figure 7). The decline observed at ODP Site 1172 is due to a drop in TOC values and LSRs. The marked rise at ACEX
is mostly driven by a peak in TOC values, from a minimum of 1.3 % (pre-PETM) to a maximum of 4.9 % (core PETM) (Elling et al., 2019). Absolute abundances of palynomorphs from ACEX suggest that the high TOC is a mixture of marine and terrestrial organic matter (Sluijs, Röhl, et al., 2008). However, both sites, with the exception of the $C_{31} S/(S + R)$ ratio at ODP Site 1172, have thermal maturity ratios that are very stable throughout the record (Figure 2–3). This indicates that although the supply of organic carbon increased during the PETM, the organic carbon source did not distinctly change. Intriguingly, there is an antiphase between $C_{30} \alpha\beta/(\alpha\beta + \beta\beta)$ and $C_{31} \alpha\beta/(\alpha\beta + \beta\beta)$ at ACEX, perhaps suggesting subtle changes in the organic carbon source during the PETM. Decoupling between the $C_{30}$ and $C_{31}$ indices could be due to a greater input of acidic peats, which are dominated by $C_{31} \alpha\beta$ hopanes but lack abundant $C_{30} \alpha\beta$ isomers (Inglis et al., 2018). The contribution of acidic peats at ACEX has also been inferred from brGDGTs (Sluijs et al., 2020).

4.3 Climate exerts primary control on OCpetro mobilisation during the PETM

Various factors may explain why shallow marine sediments are characterised by enhanced delivery of OCpetro during the PETM. Modern observations have identified a strong link between rainfall and efficient erosion/transfer of organic carbon from land-to-sea (e.g., T. I. Eglinton et al., 2021; Hilton, 2017). In the subtropics, evidence for changes in the hydrological cycle during the PETM are scarce. Previous work at TDP Site 14 revealed that the hydrogen isotope of $n$-alkanes ($\delta^2H_{n\text{-alkanes}}$) increased during the PETM, which was inferred to represent a shift towards more arid climate conditions (Carmichael et al., 2017; Handley et al., 2008). Enhanced aridity could lead to minimal vegetation cover, hindering soil development, and maximising the potential for erosion and mobilisation of OCpetro (e.g., Hilton et al., 2008; Leithold et al., 2006). Furthermore, large fluctuations in $\delta^2H_{n\text{-alkanes}}$ values may indicate oscillations between dry and wet climate states and/or an increase in extreme precipitation events (Carmichael et al., 2017; Handley et al., 2008). Modelling studies over subtropical Africa during the PETM further support the latter (Carmichael et al., 2018). Episodic and intense rainfall on a landscape prone to erosion would explain the highly variable delivery of different organic carbon sources, as shown by the hopane-based thermal maturity data (this study), $\delta^{13}C_{org}$values, and $n$-alkane $\delta^{13}C$ values (Aze et al., 2014; Handley et al., 2008).
Analogous to TDP Site 14, Kheu River also exhibits high variability in the thermal maturity ratios (e.g., CPI, C_{29} \alpha\beta/C_{30} \alpha\beta, and C_{29} \beta\alpha/(\beta\alpha + \alpha\beta); this study), chain-length distributions of \textit{n}-alkanes, BIT index, grain-size, and CIA during the PETM (Dickson et al., 2014). These features are consistent with episodic changes in precipitation, although some of the pulses at Kheu River have been argued to correlate to brief intervals of marine transgression (Shcherbinina et al., 2016). There are multiple lines of evidences associating other mid-latitude sites with increased transient and extreme rainfall events during the PETM. For example, the deposition of conglomerates in the Pyrenees (Chen et al., 2018; Schmitz & Pujalte, 2003, 2007) and changes in paleosol weathering indices and/or the abundance and composition of nodules in the Bighorn Basin (e.g., Kraus et al., 2013; Kraus & Riggins, 2007). There is also evidence for greater freshwater runoff in the Atlantic Coastal Plain (i.e., Ancora, SDB, and CamDor) during the PETM, with the development of a river-dominated shelf referred to as the “Appalachian Amazon” (Doubrawa et al., 2022; Kopp et al., 2009; Self-Trail et al., 2017). This is consistent with high-resolution climate models that suggest the western Atlantic region was dominated by an increase in extratropical cyclones and more extreme rainfall events (Kiehl et al., 2021; Rush et al., 2021; Shields et al., 2021). Although the hydrological cycle likely exerted a first-order control on the mobilisation of terrestrial organic carbon, other ecological and/or geologic controls could have also been important. For example, the dominance of OC\textsubscript{bio} at Kheu River may reflect abundant vegetation cover (e.g., Goñi et al., 2013). On the other hand, the dominance of OC\textsubscript{petro} at TDP Site 14 may reflect greater availability of OC\textsubscript{petro}-rich rock and/or exacerbated erosion of OC\textsubscript{petro} caused by limited soil and vegetation (e.g., Hilton et al., 2011).

Model simulations also indicate an increase in precipitation in the high-latitudes for a PETM-type warming event (e.g., Carmichael et al., 2016; Cramwinckel et al., 2023; Winguth et al., 2010). Proxies also reconstruct northern and southern high-latitudes to be wetter at the onset of the PETM (e.g., evidence from palynomorphs (Korasidis et al., 2022; Sluijs et al., 2006), fossilised plants (Harding et al., 2011), hydrogen isotopes of \textit{n}-alkanes (\delta^{2}H_{n-alkanes}; Pagani et al., 2006), and clay-mineralogy (Dypvik et al., 2011; Kaiho et al., 1996; Robert & Kennett, 1994)). Yet, both high-latitude sites (i.e., ACEX and ODP Site 1172) exhibit a relatively stable source of organic carbon during the PETM. This suggests that changes in seasonality and extreme precipitation events (alongside overall wetter conditions) are required to mobilise OC\textsubscript{petro} (see...
section 4.1). Alternatively, there may be other feedback mechanisms and/or more regional controls beyond the hydrological cycle. In modern systems, local geomorphic processes play a strong role in regulating OC<sub>petro</sub> transport from land-to-sea (e.g., Hilton & West, 2020). However, tectonic activity is hard to constrain in deep-time. Variability in OC<sub>petro</sub> MARs could also be attributed to changes in sea level during the PETM. Indeed, various studies have suggested marine transgression during the PETM, including: ACEX (Sluijs et al., 2006); ODP Site 1172 (Sluijs et al., 2011); Kheu River (Shcherbinina et al., 2016); the Atlantic Coastal Plain (John et al., 2008); and elsewhere (Sluijs, Brinkhuis, et al., 2008 and references therein). Although sea level rise is expected to reduce the supply of terrestrial organic carbon into the marine real, this is rarely observed (e.g., Sluijs et al., 2014) and most PETM sites are characterised by enhanced terrigenous material during the PETM (Carmichael et al., 2017 and references therein).

4.4 Timing and implications for CO<sub>2</sub> release during the PETM Enhanced OC<sub>petro</sub> delivery was suggested to have occurred ~10–20 kyrs after the onset of the PETM (i.e., within the body of the CIE) by Lyons et al. (2019). Here we confirm that elevated OC<sub>petro</sub> MARs occurred within the core of the PETM at several other sites (i.e., ACEX, Kheu River, Ancora; Figure 8). However, the exact timing within the core (i.e., onset or body) cannot be determined due to the lack of robust age constraints. The sites where the recovery phases were defined (i.e., ACEX, Kheu River, Ancora, and SDB), enables insight into whether enhanced OC<sub>petro</sub> MARs continued after the body of the CIE or recovered to pre-PETM values. Interestingly, at both Ancora and SDB, median OC<sub>petro</sub> MARs are higher than the core of the PETM in Phase II and I, respectively (Figure 8). Although an increase in OC<sub>petro</sub> MAR during the recovery is not observed at ACEX and Kheu River, values do not return to pre-PETM levels. This suggests that at certain localities, terrestrial organic carbon cycle perturbations continued into the recovery phase. If this OC<sub>petro</sub> was oxidised, it may provide an additional source of CO<sub>2</sub> during the recovery.
Figure 8: Violin plots of $OC_{\text{petro}}$ MARs (gC cm$^{-2}$ kyr$^{-1}$) for the defined time intervals of site (a) ACEX, (b) Kheu River, (c) Ancora, and (d) SDB. The thick dashed line represents the median and the thin dashed line extends from the 25th to 75th percentiles.

Overall, Lyons et al. (2019) inferred between $10^2$ and $10^4$ PgC was released as CO$_2$ globally due to oxidation of $OC_{\text{petro}}$ during the PETM. This assumed that the study sites (i.e., SDB, CamDor, and TDP Site 14) are globally representative. However, this study demonstrates that an increase in $OC_{\text{petro}}$ MARs was mostly restricted to the subtropics and mid-latitudes. In addition, the maximum value of $10^4$ PgC assumed that 85% of $OC_{\text{petro}}$ is oxidised. However, increased erosion of clastic sediments can aid the preservation of $OC_{\text{petro}}$ (e.g., Bouchez et al., 2014; Burdige, 2007). Furthermore, intense precipitation events (characteristic of the subtropics and mid-latitudes; e.g., Carmichael et al., 2017; Handley et al., 2008; Kiehl et al., 2021; Kraus et al.,
2013; Kraus & Riggins, 2007; Rush et al., 2021; Schmitz & Pujalte, 2003, 2007; Shields et al., 2021) may reduce the transfer time of OCpetro from source to sink, thereby reducing the possibility for oxidation (e.g., Hilton et al., 2011). However, it is important to consider that shallow marine sites will likely integrate an expansive catchment area, which incorporate slow meandering rivers as well as steep mountainous rivers. In the former system, the extent of OCpetro oxidised could be as high as ~90% (e.g., Bouchez et al., 2010; Galy et al., 2008). This is especially likely at sites where large freshwater input was evident, such as the Atlantic Coastal Plain (Doubrawa et al., 2022; Kopp et al., 2009; Self-Trail et al., 2017). Future work on paleo-digital elevation models may further help elucidate sediment routing systems during the PETM (Lyster et al., 2020). In conclusion, this study demonstrates that although oxidation of OCpetro likely contributed additional CO2 during the PETM, global estimates may be lower than previously inferred. We also demonstrate that CO2 release may have continued into the recovery of the PETM, suggesting that other feedback mechanisms (e.g., OCbio burial) were necessary to aid in the recovery of the Earth’s climate system.

5 Conclusion

Here, we use a multi-biomarker approach to reconstruct the mobilisation of petrogenic organic carbon (OCpetro) during the PETM. We find widespread evidence for enhanced OCpetro mass accumulation rates (MARs) in the subtropics and mid-latitudes during the PETM. In this region, we argue that extreme rainfall events exacerbated erosion, mobilisation, and burial of OCpetro in the marine realm. In addition, we demonstrate that OCpetro MARs persisted into the recovery phase of the PETM. However, the high-latitude sites do not exhibit a strong shift in the source of organic carbon. This may be due to a more stable hydrological regime and/or additional controls such as geomorphic processes or sea level change. Overall, OCpetro oxidation likely acted as an additional source of CO2 during the PETM. However, further work is needed to determine the exact contributions of OCpetro as a positive feedback mechanism during the PETM and other transient warming events.

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Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The processed data used in this study are available at OSF and associated with a CC-By Attribution 4.0 International license (Hollingsworth, 2023).

Author contributions:

Conceptualization: E. H. Hollingsworth, G. N. Inglis


Resources: F. J. Elling, A. Pearson

Visualisation: E. H. Hollingsworth

Writing – original draft: E. H. Hollingsworth
References


Bouchez, J., Beyssac, O., Galy, V., Gaillardet, J., France-lanord, C., Maurice, L., & Moreiraturcq, P. (2010). Oxidation of petrogenic organic carbon in the Amazon floodplain as a


Carmichael, M. J., Inglis, G. N., Badger, M. P. S., Naafs, B. D. A., Behrooz, L., Remmelzwaal,


Tierney, J. E., Zhu, J., Li, M., Ridgwell, A., Hakim, G. J., Poulsen, C. J., Whiteford, R. D. M.,


**References from the Supporting Information**


sequences, New Jersey Coastal Plain: Evidence for glacioeustatic control.


Hollis, C. J., Dunkley Jones, T., Anagnostou, E., Bijl, P. K., Cramwinckel, M. J., Cui, Y.,
Dickens, G. R., Edgar, K. M., Eley, Y., Evans, D., Foster, G. L., Frieling, J., Inglis, G. N.,
Kennedy, E. M., Kozdron, R., Lauretano, V., Lear, C. H., Littler, K., Lourens, L., ... Lunt,
D. J. (2019). The DeepMIP contribution to PMIP4: Methodologies for selection,
compilation and analysis of latest Paleocene and early Eocene climate proxy data,
incorporating version 0.1 of the DeepMIP database. *Geoscientific Model Development,
12*(7), 3149–3206. https://doi.org/10.5194/gmd-12-3149-2019


https://doi.org/10.1038/s41467-018-05486-w


https://doi.org/10.1016/j.marmicro.2012.05.003


